



11 Publication number:

0 426 904 A1

(12)

EUROPEAN PATENT APPLICATION

AM

(21) Application number: 89202791.3

2 Date of filing: 06.11.89

(1) Int. Cl.⁵: **B05D 5/08**, B05C 9/14, B05D 3/06, B05D 7/24, B63B 59/04, C09D 5/16

- Date of publication of application:15.05.91 Bulletin 91/20
- Designated Contracting States:
 AT BE CH DE ES FR GB GR IT LI LU NL SE
- 7) Applicant: Poullos, Mark 9935 Gooding Drive Dallas Texas 75220(US)

- 2 Inventor: Poullos, Mark 9935 Gooding Drive Dallas Texas 75220(US)
- Representative: Flamman, Han
 LIOC Patents and Licensing P.O. Box 85096
 NL-3508 AB Utrecht(NL)
- Method for applying a coating to a substrate.
- Method for applying a coating to a substrate, in particular the outer surfaces of ships' hulls in order to protect them from fouling by exposure to marine organisms in a submerged aquatic environment, whereby the coating consists of polymerized fluorocarbon material (2, 6) which is thermally fused to the substrate (4,7), for example by means of a

coherent form of radiation (1,8), e.g. a laser beam, whereby the fluorocarbon coating (2,6) absorbs sufficient energy to melt and pass sufficient energy to heat the substrate (4,7) at and near the interface (3,9), to bond the coating (2,6) and the substrate interface (3,9).

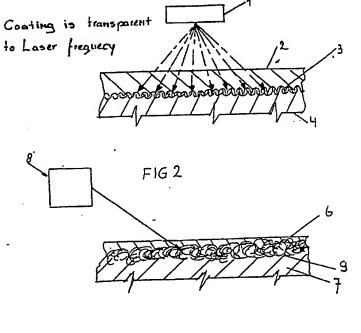


FIG 1

Xerox Copy Centre





METHOD FOR APPLYING A COATING TO A SUBSTRATE

25

The invention relates to a method for applying a coating to a substrate, in particular the outer surfaces of ships' hulls in order to protect them from fouling by exposure to marine organisms in a submerged aquatic environment.

Such methods are known from the US patent nos 3,684,752, 3,979,354 and 4,082,709 and describe the method of applying paint including a biocide, which destroys the fouling organisms with a toxic compound that is released into the water surrounding the ship. However these methods create an ecological problem in that the toxins destroy desirable organisms along with the fouling marine organisms such as barnacles, since most anti-fouling toxins are slowly and gradually released into their surrounding waters, poisoning any marine fouling organism with which it comes in contact.

The invention is characterized in that the coating consists of polymerized fluorocarbon material, preferably of the group constituted by PFA (polyfluoraether), PTFE (polytetrafluoroethylene), FEP (fluorinated ethylene propylene), CTFE (chlorotrifluoroethylene), TFE (tetrafluorethylene), ETFE (ethylenetrifluoroethylene) and PVF (polyvinylfluoride).

These materials are highly hydrophobic, thus repelling the fouling organisms and preventing them to get hold on the coating. Other advantages are their extremely smooth and non-stick surface that has a very low coefficient of friction of about 0,02 maximizing the abrasion resistance and the aqueous slip (ability of a vessel to glide through the water) and their corrosion resistance.

According to another method according to the invention, the coating is a fluorocarbon film which is thermally fused to the substrate. This has the advantage that the film as such can be without pinholes, so preventing marine organisms to attach themselves to the surface.

According to another method according to the invention, the fluorocarbon material is, as the case may be electro-statically, sprayed onto the substrate and is thermally fused to the substrate. This method is specially suited for vary large surfaces in which it is very hard to obtain the desired temperature of the substrate needed.

According to still a further method according to the invention, the thermal fusing is obtained by employing a coherent form of radiation, concentrated in a small portion of the electromagnetic spectrum, the fluorocarbon resin coating absorbing sufficient energy from the radiant laser beam to melt and, as the case may be, passing sufficient energy to heat the substrate at and near the joinder surface to approximately the same temperature, so

as to bond the coating and the substrate interface. This has the advantage that the heat needed to bond the substrate and the coating, can be locally applied and the desired temperature may be reached thereby.

According to still another aspect of the invention, the wavelengths of the coherent light source are compatible with both the fluorocarbon resin and the substrate material. In that way it is possible to heat both materials to practically the same temperature needed for fusing and adapt that wavelength to the properties of both materials.

An apparatus for carrying out the method according to the invention is characterized in that it comprises a source of coherent light. The advantage is that a relatively small size energy source can be used that is highly mobile, so that a unrealistically large oven is not required as would be in the conventional baking operations.

A further apparatus for carrying out the method according to the invention is characterized in that the source of coherent light is an infrared laser, preferably of the carbon monoxide, carbon dioxide, methane or methanol type, whose wave length is greater than one μm .

Another apparatus for carrying out the method according to the invention comprises an infrared laser, throwing its light, as the case may be via an optical system for correcting format and alignment of the beam, onto a first optical deflector which reflects a small percentage to a broad band infraRed (IR) sensor, which accurately measures the realtime IR laser power, generating a analogue or digital signal and is connected to an analogue-todigital interface circuit, on one hand linked to the central processing terminal and on the other hand to the laser power supply, locking the said laser power supply to the value specified by said central processing terminal, whereas the remaining part of the beam passes through a second optical deflector via a Y-scanner mirror and an X-scanner mirror for correct positioning of the beam during raster scanning, optical scanning correctors for keeping the beam focussed to a consisted size and angle with respect to the substrate, an IR feedback sensor receiving the IR radiation reflected from the heated substrate via the optical scanning correctors the X-scanner mirror, the Y-scanner mirror, the second optical deflector, the first optical deflector and the mirror, said IR feedback sensor generating an analogue or digital signal, being connected to another input of the analogue-to-digital interface circuit for realtime processing to correctly manage the sweep rate of the fastest moving axis (X or Y) and/or manipulate laser-power when one or the 10

15

other parameter limit has been approached, a telemetry measuring sensor, connected with its output to a third input of the analogue-to-digital interface circuit, receiving its signal from the substrate through the optical scanning correctors, the Xscanner mirror, the Y-scanner mirror and the second deflector for distance measurements to be accurately made in realtime, as the laser beam sweeps across the surface, an IR camera receiving an IR picture of the substrate and being connected with an IR thermal image processor, which is linked to a fourth input of the analogue-to-digital interface circuit. The advantage of this system is that realtime monitoring sensors are used to selectively control the infrared thermal process. This is accomplished by controlling the energy distribution precisely and accurately over the material to be irradiated, employing selective realtime thermal detectors that feed information to computerized electronics, which in turn control the power distribution such that the heating of a localized area can be precisely varied in accordance with the needs of the irradiated material. Moreover the telemetry control devices manage the optical system such that the beam spot profile remains uniform over a changing surface contour. This can be accomplished by many methods, the most preferred being a coherent light source system that monitors exact changes in the surface contour. Placing the telemetry measuring sensor in the optical path of the laser beam passed through the scanning optical correctors allows for distance measurements to be accurately made in realtime as the laser beam sweeps across the surface. Electronic signals are then sent back to the analogue-to-digital interface which in turn correctly focusses the optical scanning correctors for consistent optical focus onto the substrate. The central processing terminal then activates the shutter control circuits, which in turn open the IR laser shutters and initiates the IR laser. As the beam passes through the first optical deflector, a small percentage is reflected back to a broad band IR sensor which accurately measures realtime IR laser power. An analogue or digital signal is then generated and sent back to the analogue-to-digital conversion interface circuit where the laser power is locked into the value specified by the central processing terminal.

In still another apparatus for carrying out the method according to the invention, the telemetry measuring sensor is placed next to the optical scanning correctors for look-ahead surface profiling and storing the information in a memory, which may be incorporated in the analogue-to-digital interface circuit.

In this method look-ahead surface profiling can be done and the measurements stored in solid

state memory and recalled as a scanning laser beam reaches these points.

In a further apparatus for carrying out the method according to the invention, a carriage is present which can be moved along the substrate, having a plurality of elevator members which are interconnected by a truckframe platform, supporting the equipment necessary to carry out the previously mentioned methods.

This has the advantage that also very large objects as ships' hulls can be coated by the apparatus described above.

The invention will be illustrated by way of example, by the accompanying drawings in which

Fig.1 - shows a substrate, coated by a transparent film and bonded by laser radiation,

Fig.2 - shows a substrate on which a powdered coating is applied by electrostatically spraying and simultaneously heating both substrate and coating by laser radiation,

Fig.3 - shows a circuit for applying laser radiation to the substrate and the coating, in which realtime surface profiling is used, and

Fig.4 - a similar circuit, in which look-ahead surface profiling is performed,

Fig.5 - an apparatus wherein the laser is arranged on a vehicle.

In Fig.1 a CO₂ laser 1 throws its coherent light beam onto the preformed fluorocarbon film 2. This light beam 5 passes through the film 2 to the substrate 4 and in so doing substantially heats the substrate and the interface 3 of the transparent film 2 and substrate 4, so that the materials on each side of the interface are heated to their desired temperatures and fuse together and upon cooling the interface becomes an integral bond that permanently joins the film 2 to the substrate 4 through the now fused layer 3.

A principal use of this method is to coat the surface of a ship's hull with a thin but durable film of a fluorocarbon material that possesses an extremely smooth outer surface, which is pinhole free and has a very low water transmission rate and tenaciously clings to the ship's hull surface, so that in effect there is produced a low coefficient of friction surface that is integral with the hull, so as not to permit barnacles or other marine organisms to domicile or attach to the ship's hull and consequently, no fouling can occur, even during long periods of submersion of the hull in fresh or salt water, as would be encountered in rivers or oceans throughout the world.

Fig.2 shows how a thin coating 6 of a fluorocarbon material, particularly PTFE and PVF, in powdered form, by first spraying on the fine-powdered material through an electrostatic type of spray gun (not shown). The fluorocarbon material is fluidized in a porous bed power feed hopper and is deliv-





ered to the electrostatic spray gun in controllable volume and velocities. As the powder passes through the gun nozzle and is sprayed, it becomes electrically charged and is attracted to the grounded substrate (a ship's hull, for example) in an evenly distributed manner. The sprayed-on powder is then cured by the application of heat, or more preferably, by the application of coherent laser radiation supplied by the laser 8 that is of a wavelength or balanced wavelength, to penetrate the polymer surface with a calculated percentage absorbed in the polymer and the rest penetrating to the substrate 7 with enough remaining energy to fuse the polymer layer 6 and the adjacent substrate 7 at their interface 9.

Fig.3 shows a circuit diagram of an apparatus for applying heat to the interface of a film or powder sprayed onto the hull of a ship, for example. This apparatus comprises an Infra-Red laser 11 throwing its light via an optical system 12 for correcting format and alignment of the beam onto a first optical deflector 13, which reflects a small percentage to a broad band IR sensor 14, which accurately measures the realtime IR laser power, generating an analogue or digital signal and is connected to an analogue-to-digital interface circuit 15, on one hand linked to the central processing terminal 16 and on the other hand to the laser power supply 17 locking said laser power supply 17 to the value specified by said central processing terminal 16, whereas the remaining part of the beam passes through a second deflector 18 via an Y-scanner mirror 19 and an X-scanner mirror 20 for correct positioning of the beam during raster scanning, optical scanning correctors 21 for keeping the beam focussed to a consistent size and angle with respect to the substrate 22. The substrate 22 elevates in temperature, which in turn emits IR radiation, which is proportional to its current temperature. An IR feedback sensor 23, receiving the IR radiation reflected from said heated substrate 22 via the optical scanning correctors 21, the X-scanner mirror 20, the Y-scanner mirror 19, the second optical deflector 18, the first optical deflector 13 and the mirror 24 said IR feedback sensor 23 generating an analogue or digital signal, being connected to another input of the analogue-to-digital interface circuit 15 for realtime processing to correctly manage the sweep rate of the fastest moving axis (X or Y) and/or manipulate laser power when one or the other parameter limit has been approached. A telemetry measuring sensor 25 connected with its output to a third input of the analogue-to-digital interface circuit, receives its signal from the substrate 22 to the optical scanning correctors 21, the X-scanner mirror 20, the Y-scanner mirror 19 and the second deflector 18 for distance measurements to be accurately made in

realtime as the laser beam sweeps across the surface of the substrate 22, an IR camera receiving an IR picture of the substrate 22 and being connected with an IR thermal image processor 27. which is linked to a fourth input of the analogue-todigital interface circuit 15. This circuit passes the data in the correct format to the central processor terminal 20 where software interprets the data and then modifies the other process parameters like for example the slowest moving scan axis (X or Y), dispersion spray thickness, dispersion spray temperature, laser power distribution throughout the system, pre-heat scan temperature, post-heat scan temperature, etc. The IR camera 26 and the IR thermal image processor 27 must be set for the correct emissivity value of the surface being treated, whereas the IR sensor 23 must be set to its own correct emissivity value based on its own optical path using the IR thermal image processor system 26 and 27 as a reference point. If pre-heat scanning is to be done, then the grating tuned laser 11 should have its defraction grating set for 10,6 um wavelength. If post-heat scanning is to be done, then the grating tuned laser 11 should have its defraction grating set for a wavelength that will distribute the IR radiation between dispersion layer and substrate layer by riding the spectral transmission and absorption response curves of the dispersion layer. This in turn will allow a more equal and uniform temperature rise between coating and substrate.

The optical deflectors 13 and 18 have been specially made to be transparent to IR radiation wavelengths transmitted by the laser 11 for example 8,5 to 12 μ m, whereas the second optical deflector 18 is reflective to substrate wavelengths (2 - 8,5 μ m).

Fig.4 shows a circuit diagram of a similar apparatus, as described in Fig. 3, only the telemetry measuring sensor 25 is placed next to the optical scanning correctors 21 for look-ahead search profiling and storing the information in the memory which may be incorporated in the analogue-to-digital interface circuit 15. This information can later be recalled as the scanning laser beam reaches these points. In this apparatus the second optical deflector 18 can be dispensed with.

It has been found that with a CO or CO_2 laser, either superheterodyned or grating tuned on both with a wavelength between 4,98 μ m and 12,7 μ m or more preferred 7,0 to 12,7 μ m coupled with an accurate thermal feedback and telemetry monitoring and control system, as described in Fig. 3 and Fig. 4, is capable of controlling the thermal processing of these fluoropolymers with minimal effect to the substrate on the object being coated and that this system is also capable of compensating for the effects experienced with high power CO_2

25

35



lasers that have a multi-mode structure in the Far field, that normally cause disuniformity in thermal distribution that often renders exact and precise control useless in obtaining smooth thermal gradients and distribution. With this invention thermal distribution can be varied during the process by means of precision, power and optical adjustments.

Fig.5 shows an apparatus comprising a self-propelled vehicle 30 which can be moved along the substrate, having a very long flat bed 31 on which a superstructure 32 is mounted, having a plurality of elevator members 33 and 34, which are interconnected by a truckframe platform 35, supporting the equipment necessary to carry out the method according to the invention.

Claims

- 1. Method for applying a coating to a substrate, in particular the outer surface of ships hulls in order to protect them from fouling by exposure to marine organisms in a submerged aquatic environment, characterized in that the coating consists of polymerized fluorocarbon material, preferably of the group constituted by PFE (polyfluoraether), PTFE (polytetrafluorethylene), FEP (fluorinated ethylene propylene), CTFE (chlorotrifluoroethylene), TFE (tetrafluorethylene), ETFE (ethylenetrifluoroethylene) and PVF (polyvinylfluoride).
- 2. Method according to claim 1, characterized in that the coating is a fluorocarbon film which is thermally fused to the substrate.
- 3. Method according to claim 1, characterized in that the fluorocarbon material is sprayed onto the substrate and is thermally fused to the substrate.
- 4. Method according to claims 2 and 3, characterized in that the thermal fusing is obtained by employing a coherent form of radiation, concentrated in a small portion of the electro-magnetic spectrum the fluorocarbon resin coating absorbing sufficient energy from the radiant laser beam to melt and, as the case may be passing sufficient energy to heat the substrate at and near the joinder surface to approximately the same temperature, so as to bond the coating and the substrate interface.
- 5. Method according to claim 4, characterized in that the wavelengths of the coherent light source are compatible with both the fluorocarbon resin and the substrate material.
- 6. Apparatus for carrying out the method according to the preceding claims,
- characterized in that it comprises a source of coherent light.
- 7. Apparatus according to claim 6, characterized in that the source of coherent light is

an infrared laser, preferably of the carbon monoxide, carbon dioxide, methane or methanol type, whose wavelength is greater than 1 μ m.

8. Apparatus according to claim 7,

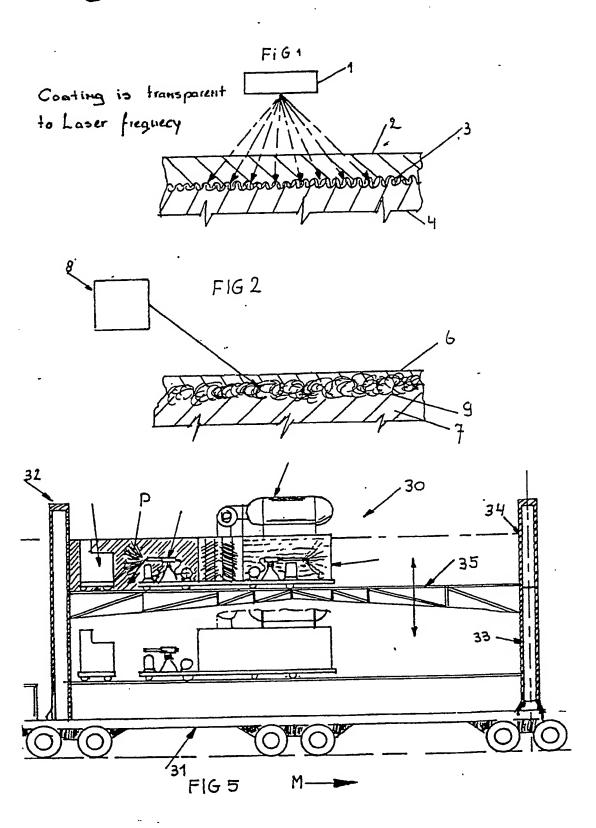
- characterized in that it comprises an infrared (IR) laser (11) throwing its light, as the case may be via an optical system (12) for correcting format and alignment of the beam, onto a first optical deflector (13), which reflects a small percentage to a broad band IR sensor (4), which accurately measures the realtime IR laser power, generating an analogue or digital signal and is connected to an analogue-todigital interface circuit (15), on one hand linked to the central processing terminal (16) and on the other hand to the laser power supply (17), locking the said laser power supply (17) to the value specified by said central processing terminal (16), whereas the remaining part of the beam passes through a second deflector (18) via an Y-scanner mirror (19) and an X-scanner mirror (20) for correct positioning of the beam during raster scanning, optical scanning correctors (21) for keeping the beam focussed to a constant size and angle with respect to the substrate (22), an IR feedback sensor (23) receiving the IR radiation reflected from the heated substrate (22) via the optical scanning correctors (21), the X-scanner mirror (20), the Yscanner mirror (19), the second optical deflector (18), the first optical deflector (13) and the mirror (24) said IR feedback sensor (23), generating an analogue or digital signal, being connected to another input of the analogue-to-digital interface circuit (15) for realtime processing to correctly manage the sweep rate of the fastest moving axis (X or Y) and/or manipulate laser power when one or the other parameter limit has been approached, a telemetry measuring sensor (25) connected with its output to a third input of the analogue-to-digital interface circuit (15) receiving its signal from the substrate (22) through the optical scanning correctors (21), the X-scanner mirror (20), the Y-scanner mirror (19) and the second deflector (18) for distance measurements to be accurately made in realtime, as the laser beam sweeps across the surface, an IR camera (26) receiving an IR picture of the substrate (22) and being connected with an IR thermal image processor (27) which is linked to a fourth input of the analogue-to-digital interface circuit (15).
- 9. Apparatus according to claim 8, characterized in that the telemetry measuring sensor (25) is placed next to the optical scanning correctors (21) for look-ahead surface profiling (28) and storing the information in a memory which may be incorporated in the analogue-to-digital interface circuit (15), whereas the second optical deflector (18) can be dispensed with.
 - 10. Apparatus according to claim 6 9,

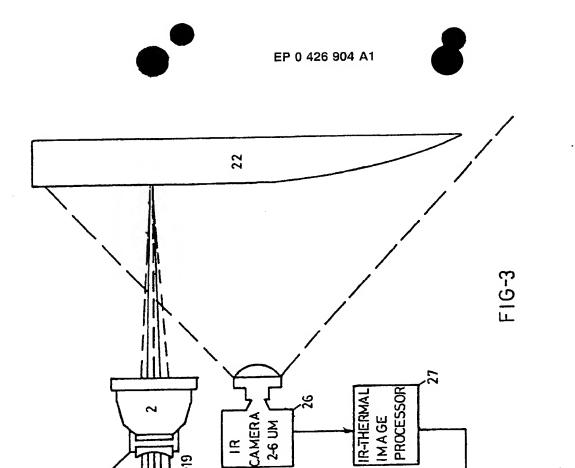




characterized in that a self-propelled vehicle (30) is present which can be moved along the substrate, having a very long flat bed (31) on which a superstructure (32) is mounted having a plurality of elevator members (33, 34), which are interconnected by a truckframe platform (35) supporting the equipment necessary to carry out the method according to the invention.







25

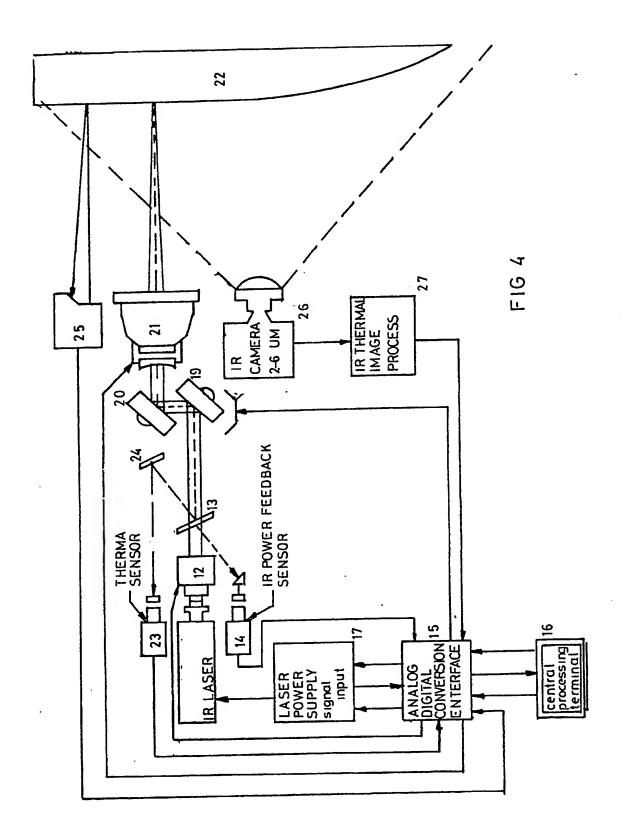
IR LASER



LASERS POWER SUPPLY & SIGNAL ANALOG & DIGITAL CONVERSION ENTERFACE

central processing terminal











EUROPEAN SEARCH REPORT

Application Number

EP 89 20 2791

Category		lication, where appropriate,	Relevant	CLASSIFICATION OF THE
	Citation of document with inc of relevant pas	sages	to claim	APPLICATION (Int. Cl.5)
x	FR-A-2 157 074 (T. * Complete document US-A-4 297 394 (B.3 * Claims; column 3,	* UNODEN et al.)	1-3	B 05 D 5/08 B 05 C 9/14 B 05 D 3/06 B 05 D 7/24
	5, lines 12-20 *			B 63 B 59/04 C 09 D 5/16
X	CHEMICAL ABSTRACTS, abstract no. 28546h, US; & JP-A-47 029 43 ELECTRIC CO., LTD) (Columbus, Uhio, 30 (FURUKAWA	1-3	
X	WORLD PATENTS' INDE) 1989, D. class A82,0 170539, Derwent Publ London, GB; & JP-A-0 IND. INC.) 02-05-198	GO2,A14, Acc. no. lications Ltd, DI 113 415 (TORAY	1	
X	125904, Derwent Pub London, GB; & JP-A-0)3,A14,P14, Acc. no. lications Ltd,)1 071 426 (A.	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	SAWASHÍTA) 16-03-198	(LATEST, week 24,	1	B 05 D 3/02 B 05 D 3/06 B 05 D 5/08
	1986, D.class A82,G 153463, Derwent Pub London, GB; & JP-A-1 KOGYO K.K.) 06-05-19	61 087 764 (DAIKIN		B 63 B 59/04 C 09 D 5/14 C 09 D 5/16
X	WORLD PATENTS' INDE: 1989, D. Class A82, Acc. no. 282520, De: Ltd, London, GB; & (DAIICHI KOGYO SEIY)	E36,F06,G02,A17,A25, rwent Publications JP-A-01 207 213		
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
TH	E HAGUE	06-07-1990	ST	ROUD J.G.
Y: pa	CATEGORY OF CITED DOCUME articularly relevant if taken alone urticularly relevant if combined with an ocument of the same category chnological background	E: earlier pater after the fill other D: document ci L: document ci	ited in the applicat ted for other reaso	ublished on, or ion





Page

Application Number

2

European Patent

EUROPEAN SEARCH REPORT

EP 89 20 2791

ategory	Citation of document with ind of relevant pass	DERED TO BE RELEVA! lication, where appropriate, sages	Rei	evant claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, abstract no. 22504y, US; Y.V. GNUSOV: "F1 for ship protection marine organisms)", (LENINGRAD), no. 2, Leningrad, USR	Columbus, Ohio, uoroplastic coating from overgrowth (by & SUDOSTROENIE	1		
X	WORLD PATENTS' INDEX class A97,C03,A14,Q2 Derwent Publications JP-A-53 113 014 (T.	4, Ass. no. 80901A, Ltd, London, GB; & YAKATA) 03-10-1978	1		
X	CHEMICAL ABSTRACTS, abstract no. 228596w US; & JP-A-61 097 37 FATS CO., LTD) 15-05	, Columbus, Unio, 4 (NIPPON OILS &	1		
X	EP-A-0 235 380 (MON * Claims; pages 2,3,	TEDISON S.p.A.) 13 *	1		TECHNICAL FIELDS
A	EP-A-0 330 237 (HÖF * Complete document	RMANN KG)	4		SEARCHED (Int. Cl.5)
A	US-A-4 411 931 (C.H. DUONG) * Complete document * DE-A-2 651 946 (CATERPILLAR TRACTOR CO.) * Claims *		4		
A			4-9)	·
A	DE-A-3 004 497 (SAI * Claims 1,2 *	ZGITTER AG) -/-	4		
	The present search report has b	een drawn up for all claims			
	Place of search	Date of completion of the search			Exember
		06-07-1990		STR	OUD J.G.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if takes alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		t document ng date ted in the ted for oth	application reason	blished on, or on s	





Page

3

Application Number



EUROPEAN SEARCH REPORT

EP 89 20 2791

	DOCUMENTS CONSIDE		Relevant	CLASSIFICATION OF THE	
Category	Citation of document with indica of relevant passage	tion, where appropriate,	to claim	APPLICATION (Int. Cl. 5)	
A	EP-A-0 202 803 (COMMO AUSTRALIA DEPT. OF IND & COMMERCE) * Claims; page 3, line	OUSTRY, TECHNOLOGY	4		
A	GB-A-2 210 291 (KANSA * Claims 1,2,15; page 11-15 *	I PAINT CO., LTD) 7, line 12; pages	4-9	-	
A	EP-A-O 168 105 (N.V. GLOEILAMPENFABRIEKEN) * Complete document *	PHILIPS'	8		
				TECHNICAL FIELDS SEARCHED (Int. Cl.5)	
	·				
	The present search report has been			Examiner	
Place of search		06-07-1990	Date of completion of the search 06-07-1990 STR		
X: y Y: p d A: to	CATEGORY OF CITED DOCUMENTS articularly relevant if taken alone articularly relevant if combined with anothe ocument of the same category echnological background ion-written disclosure attermediate document	T: theory or E: earlier pat after the fire D: document L: document	T: theory or principle underlying the inventio E: earlier patent document, but published on, after the filing date D: document cited in the application L: document cited for other reasons A: member of the same patent family, corres		